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RECENTLY PUBLISHED RESEARCH OF THE  
LENINGRAD STATE UNIVERSITY

"Hindering Action of Certain Substances on Halogen-Cleavage Reactions," N. A. Dornin, Org Chem Lab, Lenin Chem Res Inst, Leningrad State U

"Zhur Obshch Khimii" Vol 15, 1945, pp 169-72

On the basis of observations of the reaction of Na in  $\text{Et}_2\text{O}$  with  $\text{PhR}-\text{R}'\text{R}$  with additions of various substances it was shown that p-nitroaniline, hydroquinone, and maleic, phthalic, and acetic anhydrides (in descending order) hinder the initiation and progress of the reaction.  $\text{PhR}_2$ , succinic, acetic, and pseudocumenesulfonic acids,  $\text{BuOH}$ ,  $\text{Me}_2\text{CO}$ , and valeraldehyde have either no or a very slight influence.

"The Polymerisation of Styrene and Its Near Infrared Absorption Spectra." V.M. Chulanovskiy, E. P. Penkin, Phys Res Inst, Leningrad State U

"Iz Ak Nauk SSSR, Ser Fiziki" Vol 9, 1945, pp 206-10

Absorption bands of the various CH groups are most conveniently studied in the near infrared (0.75-1.0  $\mu$ ), in the second or third harmonic. In this region the band peaks are better separated than in the far infrared. The wave lengths of the absorption peaks of the CH groups are:  $\text{CH}_2 =$  8,744, 8,870, 9,170, and 9,300  $\text{\AA}$ . On polymerization of styrene, a  $\text{CH}_2 =$  group disappears and a  $-\text{CH}_2-$  group takes its place. Absorption spectra in the region of 0.85-0.97  $\mu$  were obtained for benzene, two monostyrene and

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two polystyrene specimens. The photometric curves are the better contrasted and readable, the closer the ratio of transmitted to incident light intensity is to the value  $1/e = 0.368$ ; for the absorption maximum of benzene, at about  $0.87 \mu$ , the optimum thickness of the absorbing layer is  $71 \text{ mm}$ . In general, with thickness of the absorbing layer corresponding to a transmission of from 50% to 25% of the incident intensity, more structure details can be revealed in the bands than in previous work, where considerably thinner absorbing layers were used. In the case of benzene, a small secondary absorption maximum was revealed, close and on the long-wave side of the main peak. Polystyrene samples show the expected maximum of the  $-\text{CH}_2-$  group at  $0.93 \mu$ ; the band clearly has a structure. A specimen of thick sirupy monostyrene which has undergone some degree of polymerization on long standing shows an absorption hump on the long-wave side of the aromatic peak, somewhat shifted to the short-wave side with respect to the  $-\text{CH}_2-$  band. The origin of this hump is not yet clear. It is absent in the spectrum of a sample of regular stabilized monostyrene.

"Correction for Inertia in Debye's Dispersion Formula," V. A. Dmitriev, S. B. Gurevich, Phys Inst, Leningrad U

"Zhur Eksper i Teoret Fiziki" Vol 16, 1946, pp 937-40

At high frequency, the frequency dependence of the electric conductivity  $\sigma$ , of dipolar particles is calculated by starting with the equation, based on Stoke's law for uniform rotation,  $I(d^2\theta/dt^2) = -\rho(d\theta/dt) - \mu F \sin \theta$ , where  $I$  = moment of inertia,  $\mu$  = dipole moment,  $\rho$  = coefficient of friction,  $F = F_0 e^{i\omega t}$  = internal field strength,  $\theta$  = angle between the  $\mu$  and  $F$  vectors,  $\omega$  = frequency. Hence, expanding and neglecting terms in higher powers in  $F$ ,  $d\theta/dt = -(\mu F \sin \theta) / (\rho + i\omega I)$ ; this differs from the Debye expression  $d\theta/dt = -(\mu F \sin \theta) / \rho$  by the correction term  $i\omega I$  in the denominator, allowing for inertia on rotation by the field. From the formula for  $d\theta/dt$ , the mean dipole moment  $\mu$  in the direction of  $F$  is calculated statistically and, by the Clausius-Mosotti equation,  $\epsilon'' = \mu^2 \omega^2 / 4\pi$ , where  $\epsilon''$  = the imaginary part of the complex dielectric constant;  $\epsilon''$  is expressed in terms of  $\omega$ ,  $1/T$  ( $T$  = relaxation time), and  $\rho/I$ . For dipolar particles of radius  $r = 10^{-4}$ ,  $10^{-5}$ ,  $10^{-6} \text{ cm}$ , of intramolecular densities  $d = 1$  and  $10$ , in a nonpolar liquid medium of the viscosity of water, theoretical graphs of  $\epsilon''$  against  $\log \omega$  show a steep rise, followed by a level maximum extending over a considerable range of frequencies, followed by a steep fall; example, particles of  $r = 10^{-5} \text{ cm}$ ,  $d = 10$ , interval of constant  $\epsilon''$  from  $\log \omega = 3$  to  $8$ . This contrasts with Debye's derivation which leads only to a constant level without fall at high  $\omega$ . The formula is of interest for colloidal particles and possibly macromolecules.

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"Depolarization of Light Scattered by Polystyrene,"  
E. Frisman, V. N. Tsvetkov, Leningrad State U

"Acta Physicochimica URSS" Vol 21, 1946, pp 188-9

The depolarization of light scattered at right angles by polystyrene was studied as a function of time of polymerization. For the first 8-10 hours, depolarization remained constant. Thereafter, a sharp decrease was observed in  $\rho_{\parallel}$  and  $\rho_{\perp}$  (the natural and vertically polarized incident beams) followed by a gradual increase. Throughout the experiment  $\rho_{\parallel}$  (the horizontally polarized beam) remained equal to 1. The results are interpreted as indicating that the macromolecules play an important part in the scattering and are optically much less anisotropic than the monomeric molecules. The constancy of  $\rho_{\parallel}$  indicates that the macromolecules are smaller than the wave length of the light.

"General Method of Preparation of 1, 3-Dienes From the Corresponding Saturated and Ethylenic Hydrocarbons," D. V. Tishchenko, Leningrad State U

"Zhur Obshch Khimii" Vol 17, 1947, pp 460-70

The method is based on the preparation of chlorides (from either saturated or unsaturated hydrocarbons), followed by treatment of the latter, mixed with steam, with catalysts composed of chlorides or sulfates of Ca and Mg (or both). Steam is not only a diluent which dispenses with vacuum operation, but the water condensing in the cooler portion of the apparatus absorbs HCl and prevents its reaction with the diene; it also enters the reaction, as certain amounts of ketones always form, evidently after rearrangement of the corresponding glycol, unsaturated alcohol, or enol, which may arise from partial hydrolysis of the chloride used.

Full experimental details given.

"Intramolecular Rearrangements of Compounds in the Acetylene Series: II. Reaction of an Acetylenic Chloride (2-Chloro-2-Methyl-3-Pentyne) With Silver Acetate," A. I. Zakharova, Leningrad State U

"Zhur Obshch Khimii" Vol 17, 1947, pp 686-92

Powdered KOH (200 g) and 400 cc abs Et<sub>2</sub>O were saturated with stirring at 0° with MeC≡CH and the mixture was treated with 87 g Me<sub>2</sub>CO in 300 cc Et<sub>2</sub>O with continued addition of MeC≡CH (total used 22-4 g). The mixture was decomposed with ice water and the dried organic layer gave on distillation 55% Me<sub>2</sub>C(OH)C≡CMe (I), b<sub>100</sub> 80-1°, d<sub>4</sub> 0.8909, n<sub>D</sub> 1.4438, n<sub>D</sub><sup>20</sup> 1.44386 (these values agree with those of Iotisch, but differ from those of Eurd and Cohen).

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Full experimental details given.

The same product was obtained when 42 g AgOAc in 50 cc AcOH was treated over 0.5 hour with stirring with 29 g 2-chloro-2-methyl-3-heptyne (II) in 25 cc AcOH, then heated 4 hours to 60°, diluted with water, neutralized with 10% Na<sub>2</sub>CO<sub>3</sub>, extracted with Et<sub>2</sub>O, and distilled. When the latter experiment was repeated using Pb(OAc)<sub>2</sub>, the same result was obtained. No acetate of the allene structure was detected.

"Determination of Lead in the Presence of Barium, Strontium, Calcium, and Magnesium, III," V. P. Shvedov, Leningrad State U

"Zhur Obshch Khimii" Vol 17, 1947, pp 33-7

The possibility of separating Pb<sup>2+</sup> from Ba<sup>2+</sup> by precipitating as Pb(OH)Cl was shown by experiments with the radioactive isotope of Pb and measuring the  $\alpha$ - and  $\beta$ -radiation of the filtrates from the precipitation. Attempts to weigh the precipitate were not successful and the best analytical results were obtained in separating Pb from alkaline earths by precipitating as Pb(OH)Cl, dissolving the washed precipitate in hot, slightly acidic NH<sub>4</sub>OAc and precipitating as PbCrO<sub>4</sub>. In this way fairly accurate results were obtained.

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